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OUTGASSING OF TWO SYNTHETIC FUELS.(U)

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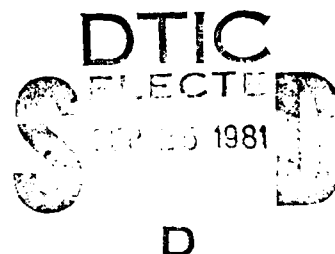
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OUTGASSING OF TWO SYNTHETIC FUELS

by
Peter Demas



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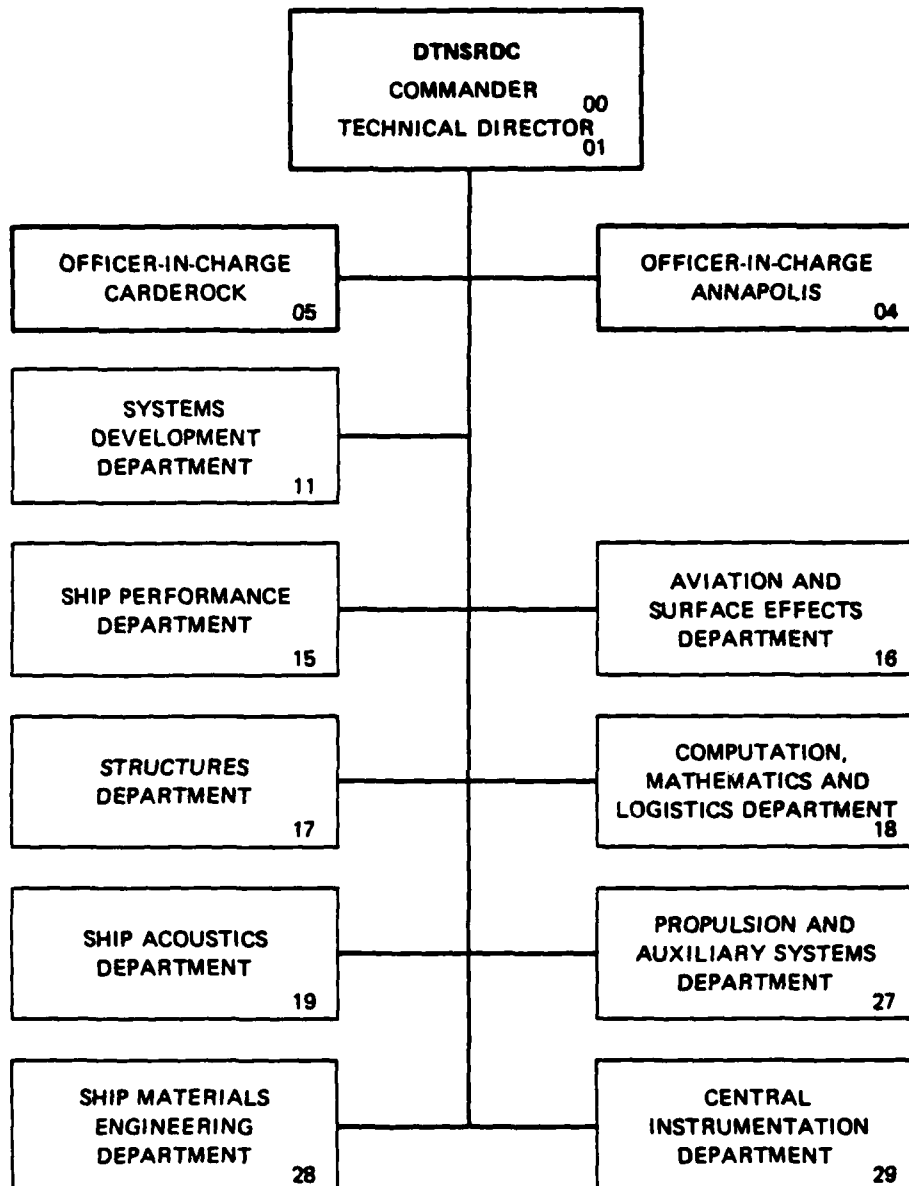
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20. Abstract (Cont.)

Single samples of each fuel were sequentially exposed to temperatures of 50°, 150°, and 250°C for 3 hours at each temperature, and the types and amounts of the outgassed products were determined.

Carbon monoxide, hydrocarbons, aldehydes, nitrogen oxides, and sulfur dioxide were outgassed. Of these, only the amount of carbon monoxide produced by diesel fuel W-375 and the amount of aldehydes produced by the conventional diesel fuel were relatively significant since each exceeded the Threshold Limit Value for these constituents by a factor of about 13. Some decomposition was evidenced when fuel W-375 was heated up to 245°C.

It is recommended that similar studies be performed with more types of synthetic fuels as these develop and become available in order to establish a better comparison of outgassing between these fuels and the conventional fuels.

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TABLE OF CONTENTS

	Page
LIST OF FIGURES	iii
LIST OF TABLES	iii
LIST OF ABBREVIATIONS	iv
ABSTRACT	1
ADMINISTRATIVE INFORMATION	1
INTRODUCTION	1
MATERIALS	2
EXPERIMENTAL PROCEDURES	7
FLUID CHARACTERIZATION	7
OUTGASSING	7
Apparatus	7
Heat Exposures and Analysis of Outgassed Products	8
Determination of Sulfur Dioxide	9
RESULTS AND DISCUSSION	9
CONCLUSIONS	11
REFERENCES	17

LIST OF FIGURES

1 - Apparatus for Heat Exposures and Collection of Water-Soluble and Water-Insoluble Outgassed Products of Synthetic Fuels	12
2 - Chromatograms of Shale Diesel Fuel W-375 (TCEP and SP2100 Columns)	14
3 - Chromatograms of Shale Jet Fuel W-383 (TCEP and SP2100 Columns)	15
4 - Chromatograms of Conventional Fuel from USS PONCE (TCEP and SP2100 Columns)	16

LIST OF TABLES

1 - Chemical and Physical Properties, SOHIO Shale Oil Demonstration Diesel Fuel Marine W-375	3
2 - Miscellaneous Analytical Data, SOHIO Shale Oil Demonstration Diesel Fuel Marine W-375	4
3 - Chemical and Physical Properties, SOHIO Shale Oil Demonstration Jet Fuel W-383	5
4 - Miscellaneous Analytical Data, SOHIO Shale Oil Demonstration Jet Fuel W-383	6
5 - Constituents Outgassed from Shale Diesel Fuel Marine W-375	9
6 - Constituents Outgassed from Shale Jet Fuel W-383	10
7 - Constituents Outgassed from Conventional Diesel Fuel from USS PONCE	10

LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
bbbl	Barrel
°C	Degrees Celsius
CS ₂	Carbon disulfide
cSt	Centistoke
EP	End point
°F	Degrees Fahrenheit
FIA	Fluorescent indicator absorption
FID	Flame ionization detector
g	Gram
GC	Gas chromatography
IBP	Initial boiling point
i.d.	Inside diameter
IR	Infrared
kg	Kilogram
l	Liter
m ³	Cubic meter
MBTH	3-methyl-2-benzothiazolinone hydrazone hydrochloride
ml	Milliliter
mm	Millimeter
NA	Not applicable
NaOH	Sodium hydroxide
nm	Nanometer
NO _x	Nitrogen oxides
o.d.	Outside diameter
p/m	Parts per million
SOHIO	Standard Oil Co. (Ohio)
SP2100	Silicone-type separation column
TCEP	1,2,3-tris(2-cyanoethoxy) propane separation column
TLV	Threshold limit value
TWA	Time-weighted average
wt	Weight
μg	Microgram

ABSTRACT

The outgassing characteristics of two synthetic fuels proposed for Navy use were investigated to determine whether potentially toxic gases could be released into ships' atmospheres.

The synthetic fuels studied were: (1) shale diesel fuel W-375 prepared to conform to MIL-F-16884G and (2) shale jet fuel W-383 prepared to conform to MIL-T-5624K. These outgassing characteristics of the synthetic fuels were compared to the outgassing characteristics of a conventional petroleum fuel conforming to MIL-16884G obtained from USS PONCE (LPD 15).

Single samples of each fuel were sequentially exposed to temperatures of 50°, 150°, and 250°C for 3 hours at each temperature, and the types and amounts of the outgassed products were determined.

Carbon monoxide, hydrocarbons, aldehydes, nitrogen oxides, and sulfur dioxide were outgassed. Of these, only the amount of carbon monoxide produced by diesel fuel W-375 and the amount of aldehydes produced by the conventional diesel fuel were relatively significant since each exceeded the Threshold Limit Value for these constituents by a factor of about 13. Some decomposition was evidenced when fuel W-375 was heated up to 245°C.

It is recommended that similar studies be performed with more types of synthetic fuels as these develop and become available in order to establish a better comparison of outgassing between these fuels and the conventional fuels.

ADMINISTRATIVE INFORMATION

This report is part of this Center's program to investigate potentially hazardous outgassing from ship-board materials. The work was performed under Program Element 62543N, Task Area ZF 43451001, Work Unit 2831-162. The work was sponsored by the Naval Material Command (MAT 08T23). T. Hinton was the cognizant program element administrator. The monitoring organization was the Naval Research Laboratory (Code 6180). Dr. H. Carhart was the cognizant program monitor.

INTRODUCTION

Outgassing due to heating of organic materials used in ships and submarines is one of the major contributors of potentially hazardous contaminants in breathing atmospheres. Since knowledge and control of outgassing characteristics of organic materials is important to the safety of the crew, this Center has been investigating emissions from organic materials exposed to elevated temperatures, below flame conditions, in the presence of large volumes of air. These conditions are characteristic of situations that would be encountered aboard ship. Gaseous emissions include volatilized components, thermal degradation products, and desorbed gases and liquids.

New ship materials are constantly being developed. They may be placed in service with emphasis on their superior performance without proper consideration of their outgassing characteristics. Materials whose outgassing characteristics were investigated at this Center in the past have included:

- Paints and adhesives.
- Thermal and electrical insulations.
- Fire-retardant materials.
- High-temperature-resistant materials.
- Hydraulic fluids.
- Lubricating oils.

This report documents an outgassing study of two synthetic fuels. They were derived from Paraho shale oil in the course of refining a 100,000-bbl* demonstration run at the SOHIO's Toledo, Ohio, refinery. In this study, one is referred to as shale diesel fuel W-375, prepared to conform to MIL-F-16884G; the other is shale jet fuel W-383, prepared to conform to MIL-T-5624K. Their outgassing characteristics were compared to the outgassing characteristics of a conventional petroleum fuel (MIL-F-16884G obtained from USS PONCE (LPD 15)).

Solid materials, such as those studied previously, do not present serious obstacles in outgassing studies since outgassing is easily controlled with respect to temperature. However, liquids, such as hydraulic fluids,^{1**} lubricating oils,² and synthetic fuels, which are the subject of this study, tend to fractionate. Due to this fractionation they cannot be subjected to temperatures higher than the boiling points of their constituents unless confined in a closed system. This report, therefore, describes the techniques used to characterize outgassing from the above synthetic fuels; they are the same techniques as the ones used in the characterization of lubricating oils.

MATERIALS

Tables 1 through 4 give some of the physical and chemical properties of the two synthetic fuels³ investigated. The diesel W-375 fuel, a clear liquid, is proposed for use in boilers, diesel engines, and gas turbines. The jet W-383 fuel, a slightly amber-colored liquid, is proposed for use in aircraft and as an alternate fuel for diesel engines and gas turbines.

* Definitions of abbreviations used are given on page iv.

** A complete listing of references is given on page 17.

TABLE 1 — CHEMICAL AND PHYSICAL PROPERTIES
SOHIO SHALE OIL DEMONSTRATION DIESEL FUEL MARINE W-375

Inspection Property	Test Result	MIL-F-16884G Requirements	ASTM Method
Color	LO.5	5 max	D 1500
Appearance	Clear/bright	Clear/Bright	—
Gravity, °API	38.2	Record	D 287
Viscosity, cSt, at 100°F (37.8°C)	2.7	1.8 - 4.5	D 445
Sulfur, % (wt)	0.02	1.00 max	D 129
Ash, % (wt)	Nil	0.005 max	D 482
Aromatics, % (vol.)	26	NA	D 1319
Olefins, % (vol.)	5	NA	D 1319
Hydrogen, % (wt)	12.78	NA	D 1018
Flash Point, °F (°C)	169 (76)	140 (60) min	D 93
Distillation Temperature, °F (°C)			D 86
IBP	406 (208)	NA	
10% recovered	455 (235)	NA	
20% recovered	473 (245)	NA	
50% recovered	509 (265)	Record	
90% recovered	563 (295)	675 (357.2) max	
EP	597 (314)	725 (385) max	
Residue + Loss, %	1.0	3.0 max	D 86
*Clear and bright and free from visible particulate matter.			

TABLE 2 — MISCELLANEOUS ANALYTICAL DATA
SOHIO SHALE OIL DEMONSTRATION DIESEL FUEL MARINE W-375

1. MAJOR ELEMENTS

Carbon (C)	<u>84.88 % (wt)</u>	Nitrogen (N)	<u>0.0033 % (wt)</u>
Hydrogen (H)	<u>12.78 % (wt)</u>	Oxygen (O)	<u>— % (wt)</u>
Sulfur (S)	<u>0.02 % (wt)</u>		

2. TRACE ELEMENTS BY EMISSION SPECTROSCOPY

Major	<u>Copper, Aluminum, Silicon</u>
Minor	<u>Magnesium, Iron, Calcium</u>
Trace	<u></u>

3. TRACE ELEMENTS BY ATOMIC ADSORPTION/OTHER QUANTITATIVE METHODS

Sodium (Na)	<u>< 1</u> p/m	Calcium (Ca)	<u></u> p/m
Potassium (K)	<u>< 1</u> p/m	Lead (Pb)	<u></u> p/m
Na + K	<u></u> p/m	Mercury (Hg)	<u></u> p/m
Vanadium (V)	<u>< 1</u> p/m	Arsenic (As)	<u>< 1</u> p/m
	<u></u> p/m		<u></u> p/m
	<u></u> p/m		<u></u> p/m

4. COMPOSITIONAL TYPES

A. FIA Analysis (ASTM D 1319)

Aromatics*	<u>26</u> % (vol)
Olefins	<u>5</u> % (vol)
Saturates**	<u>(69)</u> % (vol)

B. Acid/Base Extraction

Extracted by 2N NaOH in 67% methanol	<u>24</u> p/m (acids)
Extracted by 2N HCl in 67% methanol	<u>7.5</u> p/m (bases)

C. IR Spectrum

Similar to DTNSRDC station diesel fuel, alkanes and aromatic compounds.

5. ADDITIONAL DATA

Refractive index, n _{25/D}	<u>1.4648</u> (The light source is D line of sodium at 25°C.)
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* The aromatics volume may contain aromatic olefins, some diolefins, and compounds containing sulfur, nitrogen, or oxygen.

** By difference.

TABLE 3 — CHEMICAL AND PHYSICAL PROPERTIES
SOHIO SHALE OIL DEMONSTRATION JET FUEL W-383

Inspection Property	Test Result	MIL-F-16884G Requirements	ASTM Method
Color	LO.5	5 max	D 1500
Appearance	Clear/bright	Clear/Bright*	—
Gravity, °API	44.1	Record	D 287
Viscosity, cSt, at 100°F (37.8°C)	1.4	1.8 - 4.5	D 445
Sulfur, % (wt)	0.04	1.00 max	D 129
Ash, % (wt)	0.00	0.005 max	D 482
Aromatics, % (vol.)	23.8	NA	D 1319
Olefins, % (vol.)	1.8	NA	D 1319
Hydrogen, % (wt)	13.76	NA	D 1018
Flash Point, °F (°C)	160 (71)	140 (60) min	D 93
Distillation Temperature, °F (°C)			D 86
IBP	366 (186)	NA	
10% recovered	380 (193)	NA	
20% recovered	385 (196)	NA	
50% recovered	403 (206)	Record	
90% recovered	448 (231)	675 (357.2) max	
EP	488 (253)	725 (385) max	
Residue + Loss, %	1.4	3.0 max	D 86
*Clear and bright and free from visible particulate matter.			

TABLE 4 — MISCELLANEOUS ANALYTICAL DATA
 SOHIO SHALE OIL DEMONSTRATION JET FUEL W-383

1. MAJOR ELEMENTS

Carbon (C)	<u>86.63 % (wt)</u>	Nitrogen (N)	<u>0.0025 % (wt)</u>
Hydrogen (H)	<u>13.76 % (wt)</u>	Oxygen (O)	<u> % (wt)</u>
Sulfur (S)	<u>0.04 % (wt)</u>		

2. TRACE ELEMENTS BY EMISSION SPECTROSCOPY

Major	<u>Insufficient ash content for analysis</u>
Minor	<u>Insufficient ash content for analysis</u>
Trace	<u>Insufficient ash content for analysis</u>

3. TRACE ELEMENTS BY ATOMIC ADSORPTION/OTHER QUANTITATIVE METHODS

Sodium (Na)	<u>< 1</u>	p/m	Calcium (Ca)	<u> </u>	p/m
Potassium (K)	<u>< 1</u>	p/m	Lead (Pb)	<u> </u>	p/m
Na + K	<u> </u>	p/m	Mercury (Hg)	<u> </u>	p/m
Vanadium (V)	<u>< 1</u>	p/m	Arsenic (As)	<u>< 2</u>	p/m
	<u> </u>	p/m		<u> </u>	p/m
	<u> </u>	p/m		<u> </u>	p/m

4. COMPOSITIONAL TYPES

A. FIA Analysis (ASTM D 1319)

Aromatics*	<u>23.8</u>	% (vol)
Olefins	<u>1.8</u>	% (vol)
Saturates**	<u>(74.4)</u>	% (vol)

B. Acid/Base Extraction

Extracted by 2N NaOH in 67% methanol	<u>3.5</u>	p/m (acids)
Extracted by 2N HCl in 67% methanol	<u>2.9</u>	p/m (bases)

C. IR Spectrum

Similar to a conventional jet fuel covered by MIL-T-5624J, alkanes and aromatic compounds.

5. ADDITIONAL DATA

Refractive index, n ₂₅ /D	<u>1.4492</u> (The light source is D line of sodium at 25°C.)
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* The aromatics volume may contain aromatic olefins, some diolefins, and compounds containing sulfur

** By difference.

EXPERIMENTAL PROCEDURES

FLUID CHARACTERIZATION

The two synthetic fuels and the conventional petroleum fuel were subjected to the following tests to provide an insight into their natures and characteristics and thereby provide guidance for the outgassing studies.

- a. Head space vapors of each fuel at room temperature and
- b. 2.5% solutions of each fuel in CS_2 were examined by GC procedures employing a Hewlett-

Packard model 5730A gas chromatograph with a flame ionization detector and helium carrier gas.

Different columns were used for both a. and b. The first was a 1/8-in. o.d., 12-ft stainless steel column packed with 10% TCEP* on 100/120 mesh chromosorb, programmed at 2°C/min rise in temperature from 80° to 100°C; the second was a 1/8-in. o.d., 12-ft stainless steel column packed with 10% SP2100* on 80/100 mesh chromosorb, programmed at 4°C/min rise in temperature from 70° to 310°C. The TCEP column was selected because it can separate aliphatics from aromatics; all aliphatics up to undecane elute before benzene, thus providing an idea of the aliphatics/aromatics ratio. Because of the low heat resistance of this column (100° to 120°C), however, elution is slow for high boiling components and resolution not quite complete. For these reasons the alternate column SP2100 was also used for complete elution, better separation, and comparison. Under the conditions just mentioned, first, head space vapors from sealed containers each containing a small quantity of one fuel (part a.) and then small portions of the CS_2 solutions of each fuel (part b.) were injected into the gas chromatograph.

OUTGASSING

Apparatus

The same Center-designed-and-constructed apparatus used in the earlier outgassing studies of hydraulic fluids and lubricating oils was also employed in the study of outgassing of synthetic fuels. Referring to Figure 1a, briefly, this consists of a horizontal pyrex tube (P), 10 mm in i.d., 150 mm long and surrounded by an electric heating coil (H), wrapped with glass tape to prevent heat loss. A platinum boat (S) contains the liquid sample. The boat is inserted into the chamber through the removable Swagelock™ fitting (W). The port (J) permits withdrawal of gaseous samples directly from the chamber. The thermocouple (T), connected to a potentiometer, monitors the temperature of the sample.

*Supelco, Inc. Supelco Park, Bellefonte, PA.

For trapping water-soluble constituents such as aldehydes and NO_x in the outgassed products, two gas-scrubbing impingers (I_1 , I_2) in series, each containing 10 ml of distilled water, are connected to the heat exposure chamber. The other end of the impingers is connected through a flowmeter (F), which indicates the flow rate of air circulation, to an air circulating pump (E). The pump then is connected to the heat chamber; thus, a closed system is achieved. This is shown in Figure 1a.

A modification is made to the above apparatus to allow collection of water-insoluble gaseous products such as CO and hydrocarbons. As shown in Figure 1b, the gas-scrubbing impingers are replaced with a 5-l capacity mylar bag (D), while a tube (C) packed with molecular sieve is attached to the flowmeter end to provide pure intake air.

Heat Exposures and Analysis of Outgassed Products

The first step in the procedure to generate outgassed products is weighing an aliquot portion of the synthetic fuel under study into the platinum boat. The boat is then inserted into the heat exposure chamber, and the thermocouple is adjusted over the fuel sample. The chamber is then sealed. With the impingers in place, the air-circulating pump and the heat are turned on. The air-circulation rate is 25 ml/min. The sample is exposed stepwise for 3-hr periods to temperatures of 50°, 150°, and 250°C. Previous studies at the Center have shown a 3-hr period to be sufficient to sweep all gases that may be generated at the specified temperature out of the heating chamber. The water-soluble volatile constituents, if any, are absorbed by the scrubbing impingers as they are swept out of the heating chamber by the circulating air (Figure 1a). Impinger solutions are removed for analysis at the end of each 3-hr exposure period and replaced with new ones for the following higher temperature exposure. In this study, the impinger solutions were analyzed for the presence of aldehydes and NO_x . Aldehydes (expressed as formaldehyde) were determined by reacting 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) with a measured volume of impinger solution and measuring the light absorbance of the resulting colored solution at 628 nm.⁴ Nitrogen oxides were determined by reacting a measured volume of impinger solution with sulfamic acid and measuring the light absorbance of the resulting colored solution at 550 nm.⁵

After each of the fuels is exposed as described above, the exposure procedure is repeated using the mylar bag assembly (Figure 1b) instead of the impingers. In this study, the contents of the bag (4.5-l volume) were analyzed for CO and total hydrocarbons. Carbon monoxide was determined by catalytically converting it to methane which is then measured by GC using an FID.⁶ The total hydrocarbons (expressed as toluene) were also determined by GC using an FID.

Determination of Sulfur Dioxide

Sulfur dioxide was determined separately by outgassing the sample into a trapping solution followed by titrimetric analysis.⁷

RESULTS AND DISCUSSION

Tables 1 through 4 give some data on the physical and chemical properties of the fuels. Figures 2 through 4 are the chromatograms of each fuel obtained with columns TCEP and SP2100, respectively, from 2.5% solutions of the fuels in CS_2 . Chromatograms of the head space vapors of the same fuels are similar to these. They differ only in the percent distribution of the various components, i.e., somewhat greater percentage of lighter volatiles and a smaller percentage of heavier volatiles. The TCEP column provided the percent of lighter aliphatics present in each fuel. They are 8.77% for shale diesel fuel marine W-375, 22.33% for shale jet fuel W-383, and 5.57% for conventional fuel from USS PONCE. Aliphatics heavier than undecane that might be present, however, are not included in these percentages. Tables 5 through 7 present the constituents outgassed from the fuels.

TABLE 5 — CONSTITUENTS OUTGASSED FROM SHALE DIESEL FUEL MARINE W-375

Outgassed Constituent	Sample Weight, g	Quantity Emitted by Sample μg					Cumulative Total Emitted, g/kg	Resultant Concentration p/m per kg*	TLV ⁸
		°C							
		50	100	150	250	450			
Carbon Monoxide	0.1027	551	—	364	1,287	—	21.44	660	50
Total Hydrocarbon (as Toluene)		771	—	55	16,483	—	168.5	1578	**
Total Aldehydes (as Formaldehyde)	0.1018	0.90	—	1.1	5.8	—	0.077	2.2	2
Nitrogen Oxides (as Nitrogen Dioxide)		Nil	—	Nil	77.6	—	0.762	14.2	5
Sulfur Dioxide***	0.2078	6.2	162	13.3	34.4	45.7	1.261	17	5

* In 28.38-m³ space (10 x 10 x 10 ft).

** TLV's are not assigned to mixtures.

*** Sulfur dioxide was determined separately (see Experimental Procedures).

TABLE 6 — CONSTITUENTS OUTGASSED FROM SHALE JET FUEL W-383

Outgassed Constituent	Sample Weight, g	Quantity Emitted by Sample μg					Cumulative Total Emitted, g/kg	Resultant Concentration p/m per kg*	TLV [§]
		°C							
		50	100	150	250	450			
Carbon Monoxide	0.0838	Nil	—	Nil	Nil	—	Nil	Nil	50
Total Hydrocarbon (as Toluene)		2610	—	5107	67	—	92.9	870	**
Total Aldehydes (as Formaldehyde)	0.0892	Nil	—	Nil	Nil	—	Nil	Nil	2
Nitrogen Oxides (as Nitrogen Dioxide)		Nil	—	Nil	Nil	—	Nil	Nil	5
Sulfur Dioxide***	0.3036	7.9	4.2	4.8	53.4	30.9	0.33	4.4	5

* In 28.38-m³ space.

** TLV's are not assigned to mixtures.

*** Sulfur dioxide was determined separately (see Experimental Procedures).

TABLE 7 — CONSTITUENTS OUTGASSED FROM CONVENTIONAL DIESEL FUEL FROM USS PONCE

Outgassed Constituents	Sample Weight, g	Quantity Emitted by Sample μg			Cumulative Total Emitted, g/kg	Resultant Concentration p/m per kg*	TLV [§]
		°C					
		50	150	250			
Carbon Monoxide	0.0905	Nil	Nil	Nil	Nil	Nil	50
Total Hydrocarbon (as Toluene)		5151	4809	81	110.9	1038	**
Total Aldehydes (as Formaldehyde)	0.0841	2.4	2.47	3.12	0.96	27	2
Nitrogen Oxides (as Nitrogen Dioxide)		Nil	Nil	Nil	Nil	Nil	5
Sulfur Dioxide***	0.3262	7.8	11.7	359	1.16	15.6	5

* In 28.32-m³ space.

** TLV's are not assigned to mixtures.

*** Sulfur dioxide was determined separately (see Experimental Procedures).

The tables also show the total concentrations in parts per million of outgassed constituents that would be expected in a theoretical average shipboard space of 28.38 m^3 (1000 ft^3) if 1 kg of fuel were exposed to 250°C for a 3-hr period, the exposure period in this study. These concentrations are further compared with the threshold limit values (TLV's) of the constituents sought, which are unofficial maximum allowable concentrations of airborne contaminants. Threshold limit value/time-weighted average (TLV/TWA) is the time-weighted average concentration for a normal 8-hr work day without adverse effect. The TLV's are listed as a base line reference. Thus, it is seen from the tables that, under the experimental conditions of this study, if 1 kg of shale diesel fuel marine W-375 were placed in a 28.38-m^3 space and heated for 3 hr at 250°C , sufficient CO would be produced to exceed the TLV for CO by a factor of 13. It is also seen that, under the same conditions, SO_2 and NO_x each would exceed their respective TLV's by a factor of about 3 and that production of total aldehydes would be about the TLV limit.

Under the same conditions the conventional diesel fuel from USS PONCE would exceed the TLV for SO_2 by a factor of about 3 and the TLV for aldehydes by a factor of about 13. No CO or NO_x would be detected. Under the experimental conditions reported here, contaminants from the outgassing of shale jet fuel W-383 would not exceed their TLV's.

CONCLUSIONS

Outgassing from the three fuels investigated is relatively low. Shale jet fuel W-383 appears to outgas less contaminant than the conventional petroleum diesel fuel from USS PONCE. Shale diesel fuel marine W-375 outgassed more NO_x and CO than the conventional petroleum diesel. The conventional diesel fuel, however, outgassed more aldehydes than the shale diesel W-375. These observations are based on data derived from single determinations on a single oil sample of each type of fuel.

I_1, I_2 = MIDGET IMPINGERS WITH
 SCRUBBING SOLUTIONS
 E = CIRCULATING AIR PUMP
 F = FLOWMETER
 H = HEAT COIL
 J = SAMPLING PORT

P = PYROLYSIS CHAMBER
 S = PLATINUM BOAT FOR SAMPLE
 T = THERMOCOUPLE
 W = REMOVABLE SWAGELOCK
 FITTING

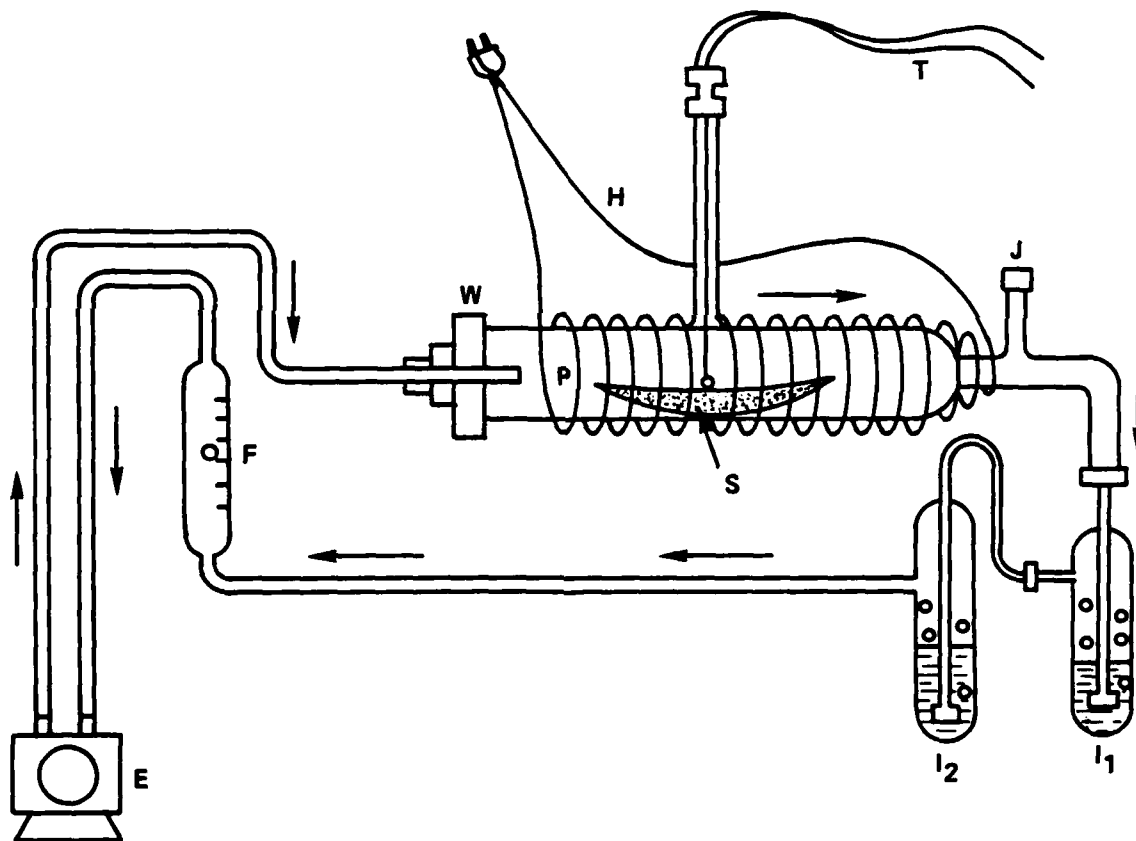


Figure 1a - Apparatus for Water-Soluble Outgassed Products

C = MOLECULAR TUBE SIEVE
 D = 5 l CAPACITY MYLAR BAG
 E = CIRCULATING AIR PUMP
 F = FLOWMETER
 H = HEAT COIL

J = SAMPLING PORT
 P = PYROLYSIS CHAMBER
 S = PLATINUM BOAT FOR SAMPLE
 T = THERMOCOUPLE
 W = REMOVABLE SWAGLOCK FITTING

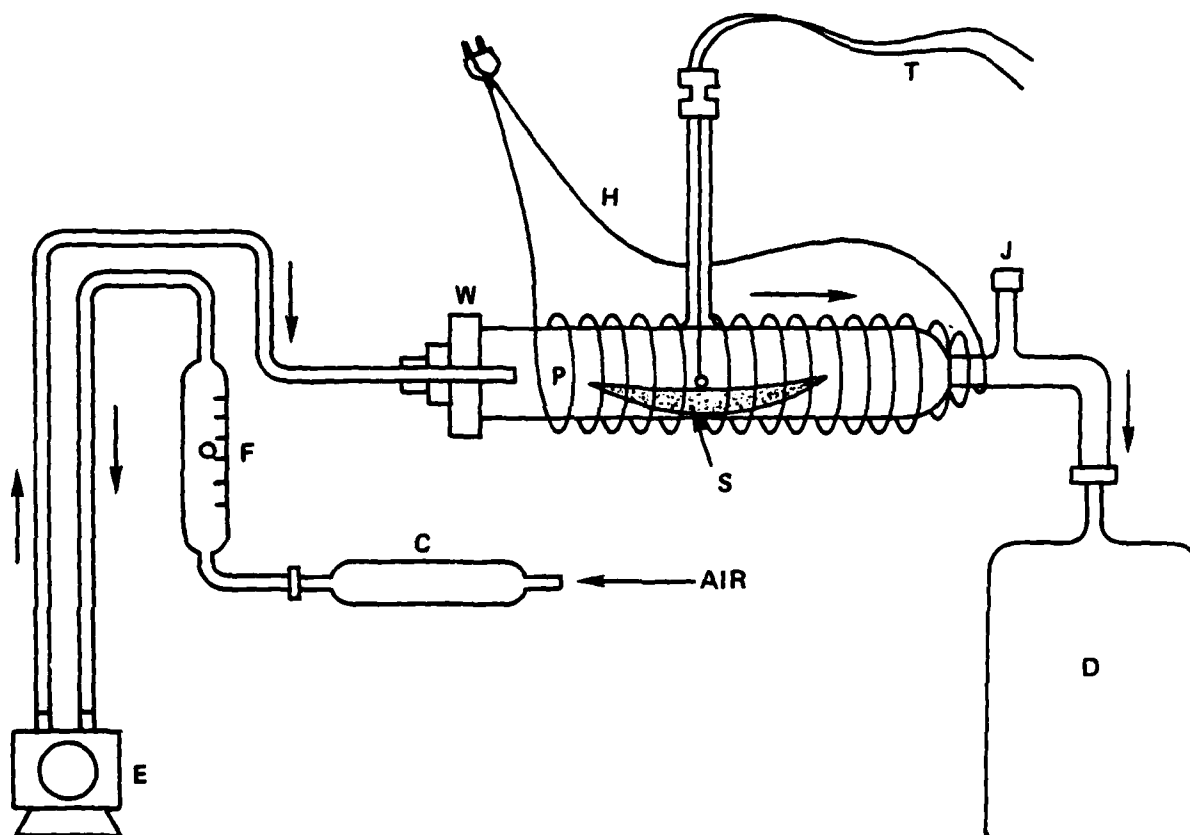


Figure 1b - Apparatus for Water Insoluble Outgassed Products

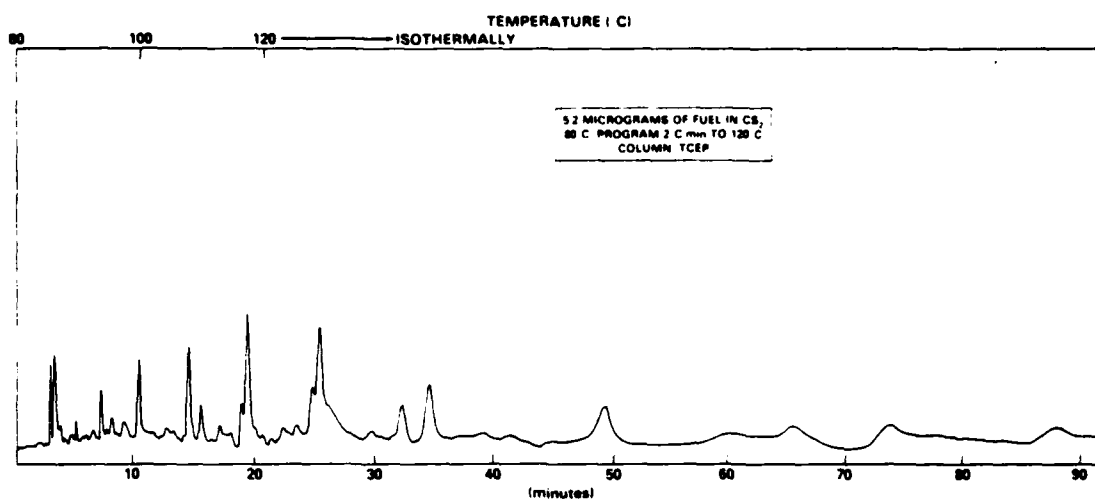


Figure 2a

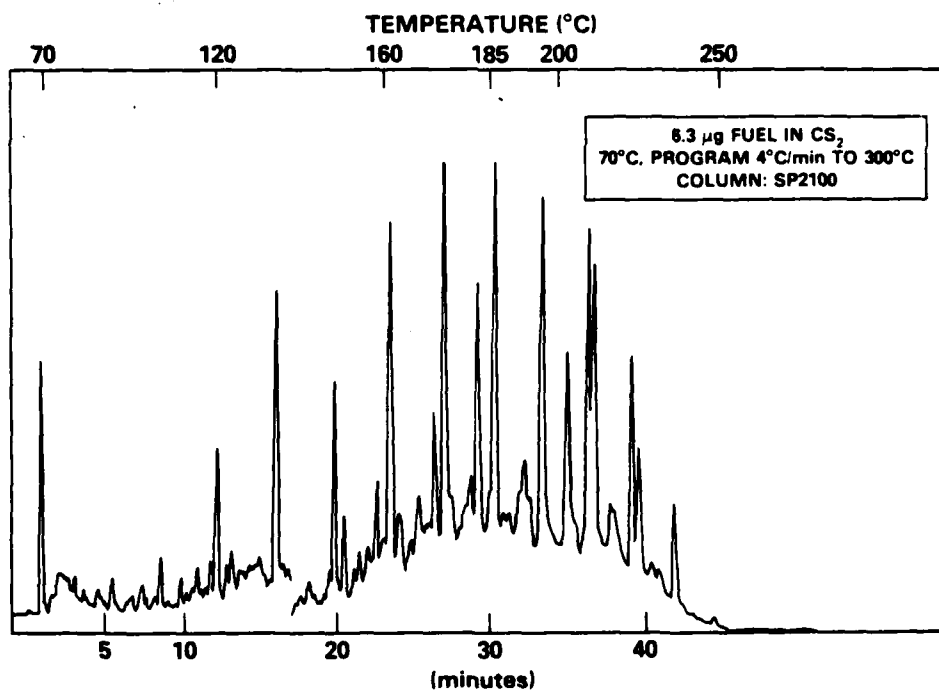


Figure 2b

Figure 2 - Chromatograms of Shale Diesel Fuel W-375
(TCEP and SP2100 Columns)

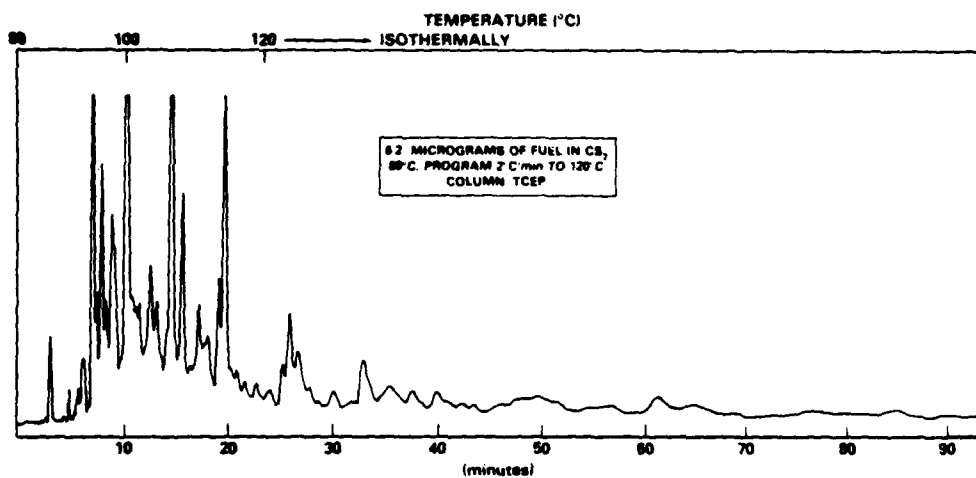


Figure 3a

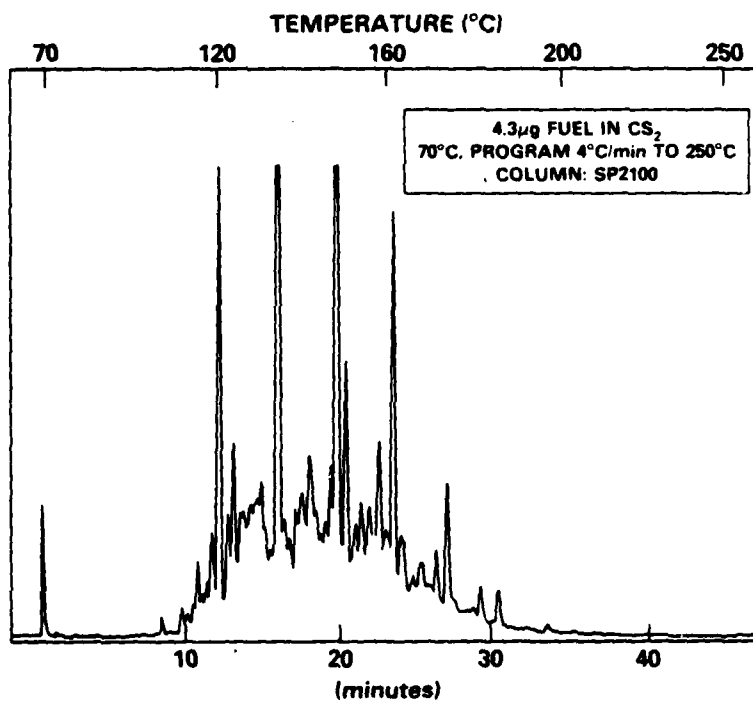


Figure 3b

Figure 3 - Chromatograms of Shale Jet Fuel W-383
(TCEP and SP2100 Columns)

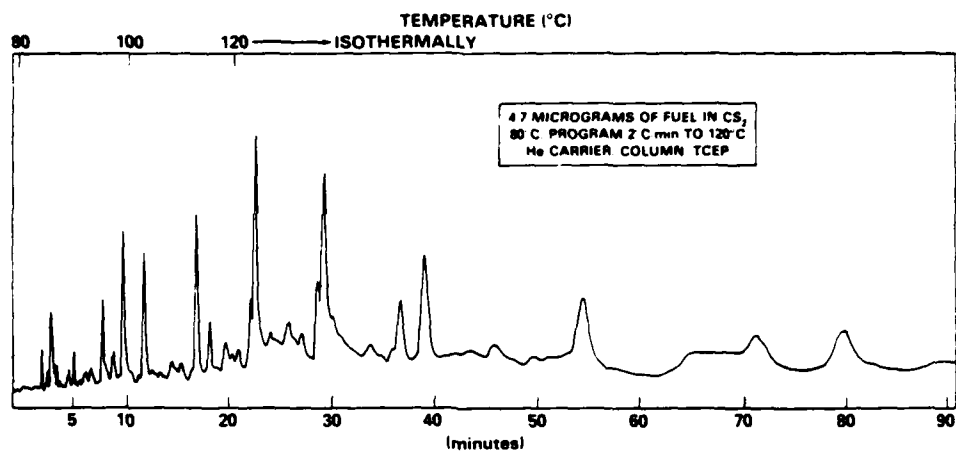


Figure 4a

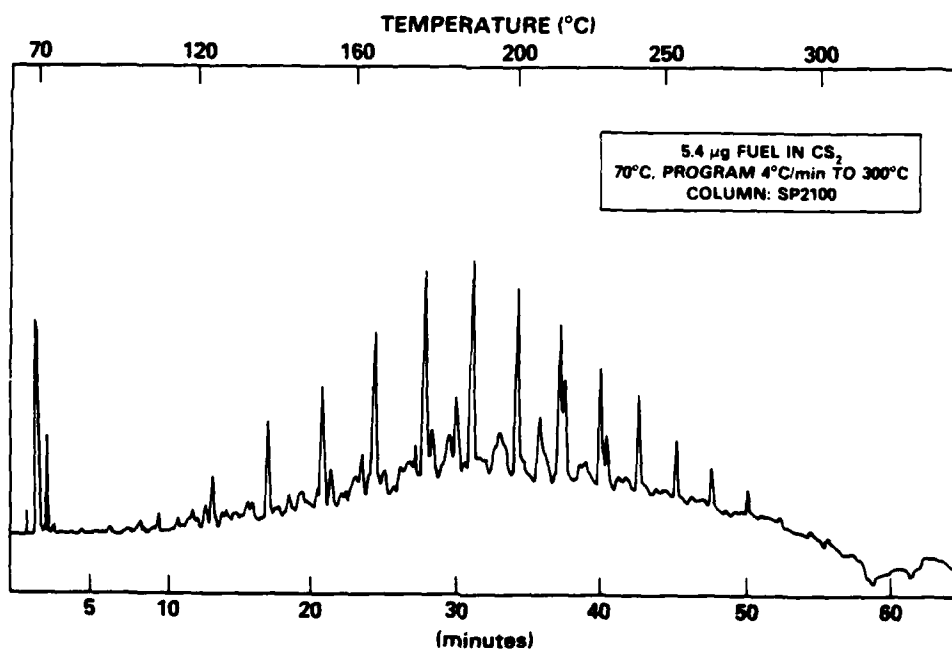


Figure 4b

Figure 4 - Chromatograms of Conventional Fuel from USS PONCE
(TCEP and SP2100 Columns)

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